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Compatibility Studies of Some Azo Polymer Blends

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ABSTRACT: Polymer blends were made by mixing the azo polymers poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene] (PDR1A), poly[4'-[[2-(methacryloyloxy)ethyl]ethylamino]-4-nitroazobenzene] (PDR1M), and poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]-3-chloro-4-nitroazobenzene] (PDR13A) with some common polymers: poly(methyl methacrylate) (PMMA), polystyrene (PS), and polycarbonate (PC). Compatibility studies of these binary blends were carried out by differential scanning calorimetry and solid-state NMR. Most of the azo polymer blends are not compatible, including PDR1A/PC, PDR1M/PC, PDR13A/PC, PDR1M/PS, PDR13A/PS, and PDR13A/PMMA blends. The compatibility of the PDR1A/PS blend could not be determined. For PDR1A/PMMA and PDR1M/PMMA blends, DSC measurements showed only one glass transition temperature for each blend. The blends were further analyzed at the molecular level by CP-MAS NMR relaxation. The slow-evaporated PDR1A/PMMA blend sample showed two separated $T_{1\rho}(^1\text{H})$ values, suggesting phase separation at the level of a few angstroms. However, compatibility could be achieved by heating the slow-evaporated blend above 110 °C. The PDR1A/PMMA and PDR1M/PMMA blends made by precipitation from methanol are also compatible. The blends which are homogeneous at the molecular level are suitable for optical storage studies. in

Introduction

Azo polymers have many special properties.¹ In the search for new materials for optical applications, such as reversible optical storage and nonlinear optical devices, azo polymers have attracted much attention.^{2,3} Polymers with low azo concentrations are particularly useful. The writing and erasing efficiency depends on the energy input from the irradiation light during the process. In principle, lower energies would be required to induce local variations of optical properties in polymers with low azo concentrations.

In order to dilute the azo content in polymer materials, copolymers⁴ and polymer blends are made. It is known that polymers with high glass transition temperatures have better long term stability of the writing information than polymers with low T_g .⁵ Polymer materials with diluted azo content can be designed to have higher glass transition temperature than those of the azo homopolymers. Another advantage is that cheap materials can be obtained from mixing the azo polymers with some conventional polymers.

The study of compatibility in polymer blends is an area of practical importance because the degree of mixing and solid-state phase structure of a blend govern its physical and chemical properties. In the case of writing and erasing information on azo polymer blends, acceptable resolutions can be achieved only on homogeneous materials.⁶ When the azo polymers are diluted with some optically inert materials, it is necessary that the blends be compatible at the molecular level to ensure the homogeneity of the material for optical studies. Dumont et al. used some azo polymer blends to study the photoisomerization of the azo group.⁷ The blends were made by mixing MMA-azo copolymers with PMMA in order to get a certain optical density and thickness. No inhomogeneities were reported. This suggests that these azo polymer blends may be compatible.

It is well known that the intimacy level of the components of a blend appears to be dependent on the method

of measurement employed in the examination. In this paper the compatibility of the azo polymer blends is studied by a combination of differential scanning calorimetry (DSC) and solid-state high resolution ¹³C-NMR spectroscopy.

DSC has been widely used to study miscibility in polymer blends. The detection of a single glass transition temperature, T_g , is generally considered as evidence of compatibility. However, DSC is only sensitive to phase sizes greater than about 10 nm.^{8,9}

The ¹³C-cross-polarization and magic angle spinning (CP-MAS) solid-state NMR technique offers an unique insight into the molecular phase structure and mobility of amorphous polymers. The parameter used to examine the blends is $T_{1\rho}(^1\text{H})$, the proton spin lattice relaxation time constant in the rotating frame.¹⁰ As a criterion for miscibility, it is superior to T_g measurements since it can be sensitive to phase sizes at levels of a few angstroms. $T_{1\rho}(^1\text{H})$ measures the efficiency of spin diffusion in a sample and depends on interproton distance and on the spectral density at the observation frequency. Strong homonuclear dipolar interaction between protons usually average the value of $T_{1\rho}(^1\text{H})$ for all the protons in a sample. When the components of the blends have two well-separated $T_{1\rho}(^1\text{H})$ values, the presence of a common $T_{1\rho}(^1\text{H})$ in their blend implies that the sample is homogeneous in the coherence scale of a few angstroms depending on the value of $T_{1\rho}(^1\text{H})$. Therefore, $T_{1\rho}(^1\text{H})$ is used to distinguish between blends that are intimately mixed and those that are not. It has been successfully used to probe molecular mixing in many polymer blends.¹¹ 13C

The present work is also a part of the investigation of the azo polymers for optical applications such as information storage. The optical properties of the blends will be reported in a forthcoming paper.⁶

Experimental Section

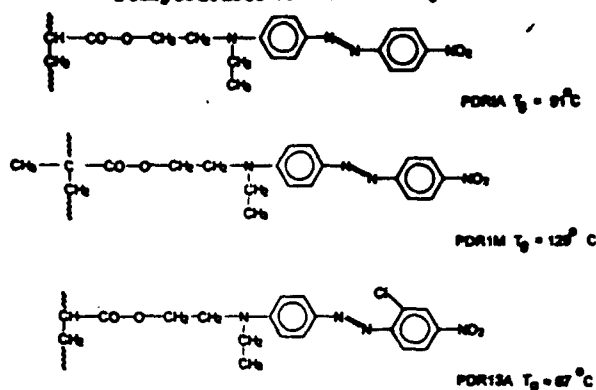
Materials. Azo polymer blends were synthesized by mixing the azo polymers poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene] (PDR1A), poly[4'-[[2-(methacryloyloxy)ethyl]ethylamino]-4-nitroazobenzene] (PDR1M), and poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]-3-chloro-4-nitroazobenzene] (PDR13A) with some conventional polymers: poly(methyl methacrylate) (PMMA), polystyrene (PS), and polycarbonate

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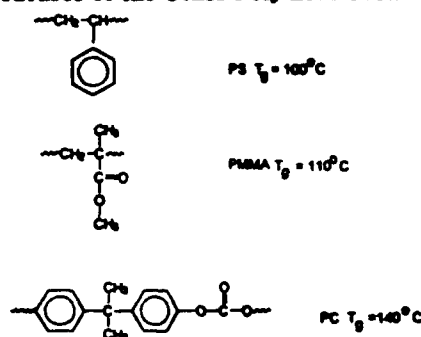
² Royal Military College.

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Scheme 1. Structure and Glass Transition Temperatures of the Azo Polymers



Scheme 2. Structure and Glass Transition Temperatures of the Other Polymers Used in Blends



(PC). The structures and the glass transition temperatures of the materials used are listed in Scheme 1 for azo polymers and Scheme 2 for the other polymers. Monomers and homopolymers PDR1A, PDR1M, and PDR13A were prepared as described in previous publications.³ PMMA (Aldrich, medium molecular weight), PS, and PC (Aldrich) were used as received.

Polymer blends were obtained by mixing solutions of the polymer pairs in hot THF with stirring, followed by slow evaporation in beakers. This low evaporation method is also used in preparing thin films for optical studies. Fifty percent by weight amounts of the azo polymers were used for blends with PC, PS, and PMMA for initial thermal analysis.

On the other hand, 12.5, 25, 37.5, 50, 62.5, 75, and 87.5 mol % PDR1A/PMMA blends were prepared by precipitation of THF solutions into methanol. After filtration, the precipitated samples were dried in vacuum for several days at $\sim 80^\circ\text{C}$ previous to thermal tests and CP-MAS ^{13}C -NMR analysis. The composition of one of the precipitated blends (50%) was checked by NMR spectroscopy in CDCl_3 . The result showed no change in the composition after precipitation.

Analysis. The glass transition temperature, T_g , was measured using differential scanning calorimetry on a Mettler TA3000 system at a scanning rate of $20^\circ\text{C}/\text{min}$. In order to ensure reproducibility, samples were subjected to at least three heating scans in succession over the temperature ranges 40 – 160°C . T_g was taken as the peak of the first derivative curve of the second or third heating scan. The glass transition temperatures of the homopolymers used are listed in Schemes 1 and 2 together with the structures.

The ^{13}C solid-state NMR measurements were made on Bruker CXP-200 instrument operating at 200.044445 and 50.307 MHz for ^1H and ^{13}C NMR, respectively. The ^{13}C spectra were collected using the methods of cross-polarization, magic angle spinning, and dipolar decoupling (CP-MAS/DD). Two pulse sequences have been developed to measure the proton spin-lattice relaxation time constant in the rotating frame $T_{\rho}(\text{H})$ by CP-MAS NMR.¹² One includes a variable contact (CP) time, while the other uses a variable delay followed by a fixed contact time. For the polymers we tested, the $T_{\rho}(\text{H})$ values are shorter than their corresponding $T_{\rho}(\text{C})$ values.¹² Hence, we can apply either of the two sequences

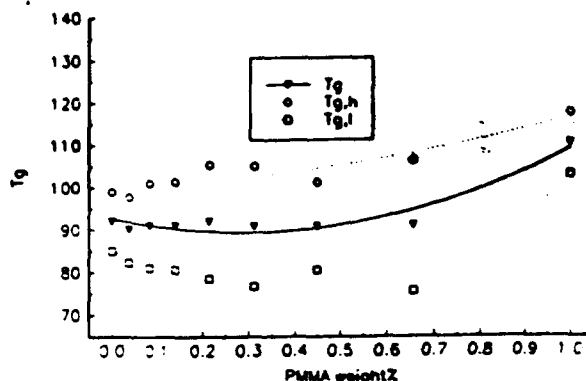


Figure 1. Glass transition temperatures of PDR1A/PMMA blends vs wt % of PDR1A.

Table 1. Glass Transition Temperatures of the Azo Polymer Blends

	PC	PS	PMMA
PDR1A	96 and 143	116	106
PDR13A	90 and 140	92 and 106	95 and 107
PDR1M	112 and 148	110 and 130	108

since they are equivalent. For most of the samples, $T_{\rho}(\text{H})$ was measured using a pulse sequence with a 90° ^1H pulse of $3.7\ \mu\text{s}$, a fixed contact time of 2 ms, and 8-s recycle delay between pulses, and a variable delay from 0.25 to 20 ms. All spectra were acquired for more than 1000 scans. The ^{13}C chemical shift values were referenced according to the ^{13}C spectra of the homopolymers in CDCl_3 solution.⁷ The $\ln(\text{peak intensities})$ of different carbon signals were plotted as a function of delay time. The $T_{\rho}(\text{H})$ values were obtained from the negative reciprocal of the slope.

Results and Discussion

Thermal Analysis. DSC measurements of the homopolymers showed only the glass transition temperatures and no other enthalpy changes before decomposition. All the polymers and blends used in this study were amorphous as confirmed by polarized microscopy.

Two well-separated glass transition temperatures were observed for PDR1A/PC, PDR1M/PC, PDR13A/PC, PDR1M/PS, PDR13A/PS, and PDR13A/PMMA blends. The two temperatures for each blend were close to the T_g values of the two corresponding homopolymers. The DSC results indicate that these blends are incompatible, therefore no further tests were carried out. The DSC results for the blends tested are listed in Table 1.

PDR1A/PMMA, PDR1A/PS, and PDR1M/PMMA blends show only one T_g . A single glass transition temperature may be an indication of miscibility at the level of about 10 nm. However, the differences between the glass transition temperatures of the component polymers are less than 20°C . In these cases, the single T_g may be a result of the poor resolution of the DSC analysis.

DSC studies show that the PDR1A/PMMA blends possess a single T_g at any composition. The DSC data of the series of blends is plotted as a function of weight fraction of PMMA in the blends in Figure 1. In order to study the broadening of the T_g range, we measured $T_{g,h}$ and $T_{g,l}$ values at the half height of the first derivative curves as shown in Figure 2. The $T_{g,h}$ and $T_{g,l}$ values are also plotted in Figure 1. The T_g transitions are broader for the blends than for the homopolymers. In fact, the glass transition curves of the blends cover the range of T_g of both PMMA (110°C) and PDR1A (91°C). This broadening of the T_g transition is known not only for incompatible blends but also for compatible blends.¹⁴

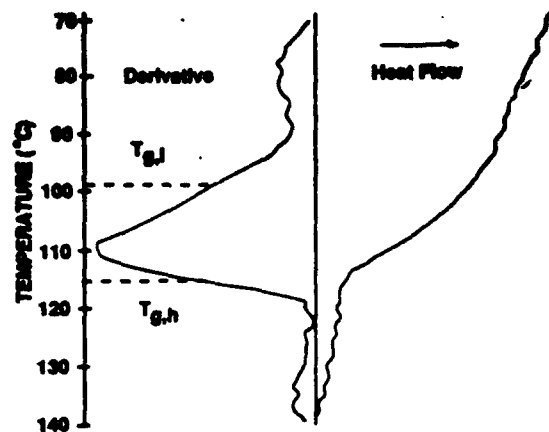
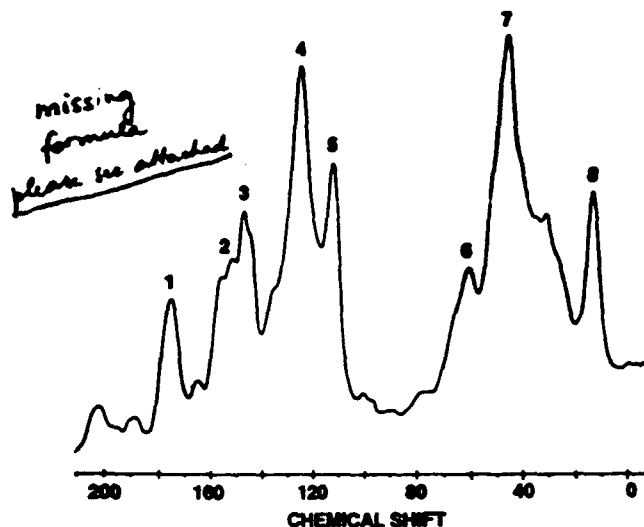


Figure 2. DSC curve (right) and first derivative (left) of PMMA.

Figure 3. CP-MAS ^{13}C -NMR spectrum of 50 mol % PDR1A/PMMA blend prepared by precipitation method.

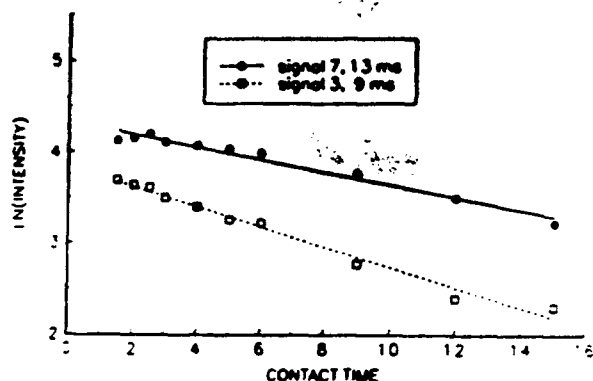
Therefore it is difficult to tell whether the PDR1A/PMMA blends are compatible or not from the DSC.

NMR Relaxation Studies. For $T_{1\rho}(\text{H})$ to be used as a criterion of miscibility, the components of the polymer blends have to have two separated $T_{1\rho}(\text{H})$ values. The blends can then have two $T_{1\rho}(\text{H})$ values similar to those of the two components when the two components form separate phases, or just one $T_{1\rho}(\text{H})$ when the blends are miscible. In the case of PDR1A/PS blend, the $T_{1\rho}(\text{H})$ values of PS and PDR1A are 7 and 6 ms, respectively.¹² They are too close to be distinguished in the blends. We found that PMMA has a $T_{1\rho}(\text{H})$ value of 25 ms, which is quite different from that of PDR1A (10 ms). Therefore, PDR1A/PMMA blends were investigated by NMR.

Figure 3 presents a typical CP-MAS ^{13}C -NMR spectrum of a PDR1A/PMMA blend (50 mol %) together with the assignments. There are some resonances in the spectrum of the polymer blend that come from only one component, the aromatic carbons of PDR1A. Signals from PMMA alone are not available. For each resolvable signal the $T_{1\rho}(\text{H})$ values were measured.

Figure 4 shows the magnetization for signal 3 (from PDR1A only) and signal 7 (from both PMMA and PDR1A) as a function of delay time for the slow-evaporated sample. The $T_{1\rho}(\text{H})$ results are listed in Table 2 for blends and homopolymers.

Two different $T_{1\rho}(\text{H})$ values (9 ms for PDR1A and 13 ms for the overlapped signals) were obtained from the spectra of the slow-evaporated blend sample (50 wt % of

Figure 4. Plot of $\ln(\text{intensity})$ as a function of delay time for signals 3 and 7 shown in Figure 2.Table 2. $T_{1\rho}(\text{H})$ Values (ms) Calculated from the Signals Shown in Figure 3 for PMMA, PDR1A, and Their Blends

sample	signal					
	1	2	4	6	7	8
PDR1A	11	11	10	10	10	11
PMMA	25			25	25	25
blend-slow evaporated	13	9	9	13	13	13
blend-slow evaporated and then heated above T_g	9	7	8	9	8	8
blend-precipitated	9	7	7	8	9	8

PDR1A). This may indicate phase separation in this blend. Because of this preparation method, the sample could not be dried very well. THF solvent peaks were clearly present in the spectra (two peaks at about 30 and 70 ppm). The blend was then heated above the glass transition temperature (110 °C) in the rotor for about 1 h under spinning and then tested again. The spectrum showed that the blend was now dry. This time, similar $T_{1\rho}(\text{H})$ values were obtained from all signals, as listed in Table 2, which indicated that the blend became compatible after heating. The phase separation in the slow-evaporated blend sample may be due to the presence of solvent, or the presence of solvent may generate different $T_{1\rho}(\text{H})$ values.¹⁵ Heating of these samples clearly produces compatible blends. Another sample (50 mol % of PDR1A) obtained by precipitation was also analyzed by solid-state NMR. The results are shown in Table 2. Similar $T_{1\rho}(\text{H})$ values were also obtained for all signals in the blend, with an average value of about 8 ms. The spin diffusion distance (x) can then be estimated using the formula¹⁶

$$x = \left(\frac{D T_{1\rho}}{2} \right)^{1/2}$$

where D is the spin diffusion constant (with the largest D s in organic system for alkanes, $6.2 \times 10^{-12} \text{ cm}^2/\text{s}$).⁷ For $T_{1\rho}(\text{H}) = 8 \text{ ms}$, x is $2.6 \times 10^{-7} \text{ cm}$. This means that the domain size in the polymer blends is probably less than 3 nm and the PDR1A/PMMA polymer blends are compatible at this level.

The compatibility of the PDR1M/PMMA blend was also checked by solid-state NMR. The sample with 50 mol % PDR1M was precipitated from a nonsolvent (methanol) and then heated above the glass transition temperature (129 °C). The signals showed a consistent $T_{1\rho}(\text{H})$ value of 4 ms, which indicated that the PDR1M/PMMA blend is also compatible at the molecular level.

It is well known that when two polymers are blended, the most likely result is a two-phase material as can be predicted from thermodynamics considerations.¹⁰ The compatibility of various methacrylate and acrylate homopolymer blends has been analyzed in the literature. It

has been shown that the structural difference of the α -methyl group is sufficient to limit monophasic behavior of the blends.¹⁷ Only a few compatible methacrylate or acrylate polymer pairs can be found in the literature.¹⁸ There may be two explanations for this unexpected compatibility. The first explanation usually involves some kind of nonbonding interactions which may be present in the system and which provide the driving force for compatibility. Ion-ion, ion-dipole, dipole-dipole, hydrogen-bonding, or charge-transfer interactions are known to perform this role. In the systems presented here such interactions are unlikely. Infrared spectra did not reveal any changes in absorbance bands which could have been related to such interactions. Indirect evidence of weak interactions can be given by chemical shifts in CP-MAS ¹³C-NMR spectra¹¹ or even by a decrease in $T_{1\rho}(^1\text{H})$ values for the two components due to a more efficient spin diffusion between closely interacting components.¹⁹ For these pairs, no chemical shifts could be observed in the solid state, and the difference in $T_{1\rho}(^1\text{H})$ values of the blend (8 ms) and the fastest relaxing component (10.5 ms for PDR1A) is too small to suggest any interaction. Hence, with the available experimental techniques, no evidence of interaction could be found. In terms of this first explanation, the compatibility here could be considered an anomaly, as in the case of polystyrene-poly(phenylene oxide) blends.

The second explanation would take into account the relatively low molecular weights of both PDR1A and PDR1M (ca. 10–12 structural units).³ It is well known that miscibility can be greater for lower molecular weight polymers and oligomers, because the entropic factor may still be important. Hence, in terms of this second explanation, the analysed pairs may be compatible only at these relatively low molecular weights and behave "normally" (i.e., become incompatible) at higher molecular weight. This has still to be investigated, since we were not successful yet in preparing higher molecular weight azo polymers.

In any case, the real explanation for the compatibility of these systems is probably a combination of these two explanations: these are rare systems which are compatible at the molecular level at least in the range of low molecular weights.

Conclusions

Two separated T_g values were observed for most of the azo polymer blends tested, except for the PDR1A/PMMA, PDR1A/PS, and PDR1M/PMMA blends.

Blends of PDR1A/PMMA can form homogeneous films by solution casting and heating. PDR1A/PMMA blend samples prepared by the slow evaporation method showed separated $T_{1\rho}(^1\text{H})$ values which may indicate separated phases. However, homogeneous polymer blends could be obtained by either heating the samples above the glass transition temperature or by precipitation into a nonsolvent.

The casted and then heated films of the PDR1A/PMMA blends are suitable for use in the optical storage tests.¹⁶ The azo polymer blends with low azo concentration are very interesting because there is no optically inert neighboring group around the azo groups. In fact, the writing and erasing results will be compared with two other series of random copolymers made from disperse red 1 and methyl methacrylate to study the effect of the nearest neighbor in the polymers.¹⁶

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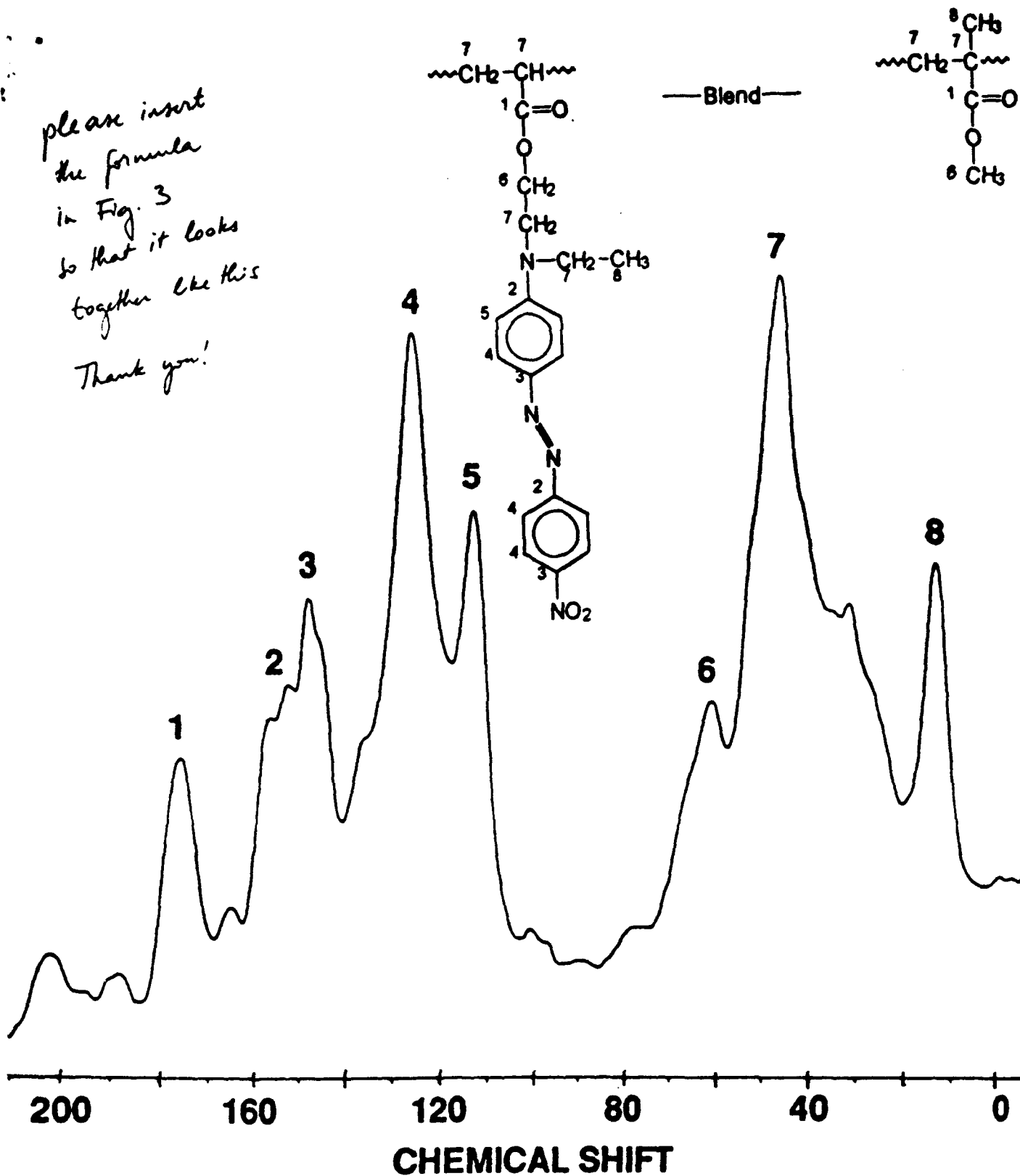


Fig. 3 5/2